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Infrared Emission Measurements of Morning Stratospheric N_2O_5

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Infrared emission spectra obtained during a balloon flight of the Air Force Geophysics Laboratory SCRIBE system by the University of Denver are used to measure stratospheric N_2O_5 after sunrise over New Mexico (latitude 33°N). This is the first daytime measurement of N_2O_5. Comparisons with photochemical modeling show consistency between the observed and predicted decline of N_2O_5 during the morning hours.

INTRODUCTION

N_2O_5 is an important stratospheric reservoir species for NO_x, produced during the night by the reactions

$$NO_2 + O_3 \Rightarrow NO_3 + O_2 \quad (1)$$

$$NO_3 + NO_2 + M \Rightarrow N_2O_5 + M \quad (2)$$

After sunrise, N_2O_5 gradually photolyzes back into NO_2:

$$N_2O_5 + h\nu \Rightarrow NO_2 + NO_3 \quad (3)$$

$$N_2O_5 + h\nu \Rightarrow 2NO_2 + O \quad (4)$$

The diurnal variation of stratospheric N_2O_5, as computed in photochemical models [*Brasseur and Solomon*, 1984], is a periodic function; it decays due to photolysis after sunrise and increases through reaction (2) at night.

Nighttime N_2O_5 was tentatively observed by *Roscoe* [1982] and *Evans* [1986]. A definitive observation of N_2O_5 was made by *Toon et al.* [1986] and *Toon* [1987], who observed the ν_{12} band (~1230–1260 cm^{-1}) and the ν_1 and ν_{11} bands (~1680–1770 cm^{-1}) in transmission spectra obtained with the ATMOS instrument at sunrise. Recently, *Kunde et al.* [1988] have measured nighttime N_2O_5 from infrared emission spectra in the ν_{12} region.

In the present work, infrared emission data are analyzed to demonstrate the first measurement of daytime N_2O_5, and the results are compared with the predictions of a one-dimensional photochemical model.

OBSERVATIONS

The data were obtained during a balloon flight of the Air Force Geophysics Laboratory (AFGL) SCRIBE system (Stratospheric Cryogenic Interferometer Balloon Experiment) by the University of Denver from Roswell, New Mexico, on July 5, 1984. The instrumentation consisted of a LN_2-cooled Michelson interferometer system employing cat's eye optics and having a maximum path difference of ~9 cm. The time for a single scan was ~30 s, including a 5-s fly-back. The field of view was ~0.8°. Data for the radiometric calibration of the emission spectra were recorded during the flight by occasionally moving an on-board black body into the instrument field of view. For a detailed discussion of the SCRIBE instrumentation, see *Murcray et al.* [1984].

The balloon was launched at 0610 MDT (Mountain Daylight Time), and reached a float altitude of 30.6 km at 0740 MDT. Data were recorded at a number of zenith angles. Of these, the scans at 90.6° and 91.1° were selected as most suitable for the detection and measurement of daytime N_2O_5. The 90.6° data displayed here are actually the average of 14 individual scans selected from those recorded between 0751 and 0759 MDT, while the 91.1° data are the average of 12 scans recorded during the interval 0916–0923.5 MDT. Sunrise occurred at the balloon float altitude at approximately 0530 MDT, and at ground level at the local time of 0456 MST (Mountain Standard Time).

ANALYSIS AND RESULTS

The data were analyzed by comparison with synthetic spectra generated using a line-by-line computer program developed at the University of Denver. The program, which takes refractive effects into account through a ray-tracing routine, calculates transmittance or emission over a user-selected number of atmospheric layers at a net interval of 0.001 cm^{-1}. The 1986 edition of the HITRAN data base [*Rothman et al.*, 1987] is used as input to the program. Line parameters for N_2O_5 do not exist, but the absorption coefficients needed to compute the N_2O_5 contribution to the atmospheric emission are generated by the program using the absorption cross sections for N_2O_5 which are also included in the HITRAN data base. Finally, the computed radiances are degraded in resolution by convolution with an appropriate instrument line shape function.

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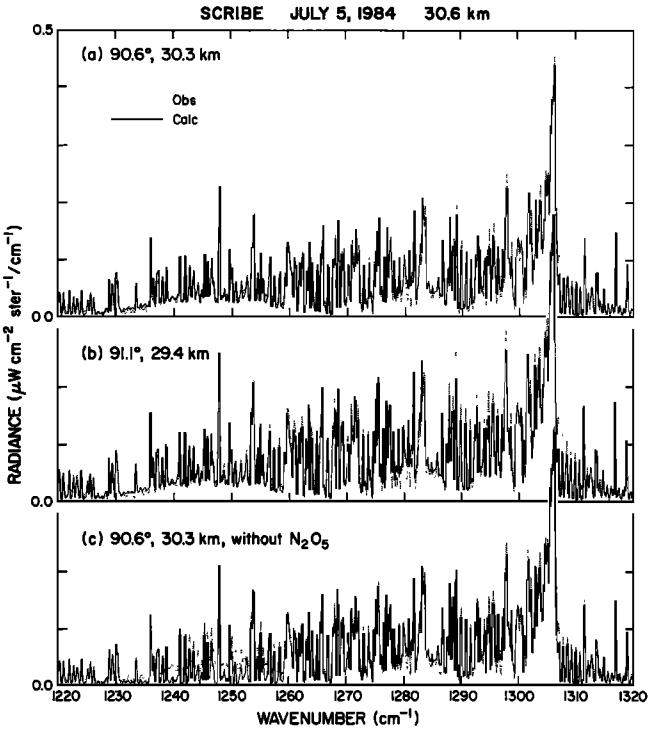

Fig. 1. Comparisons of observed (dotted curves) and calculated (solid curves) atmospheric emission spectra in the 1220–1320 cm^{-1} region. The spectra were obtained during a balloon flight made on July 5, 1984, by the University of Denver with the AFGL SCRIBE system from balloon float altitude of 30.6 km. Zenith angles and tangent altitudes are indicated in the figure. The top two frames include N_2O_5 in the spectral calculations while for the bottom frame N_2O_5 was excluded from the calculation.

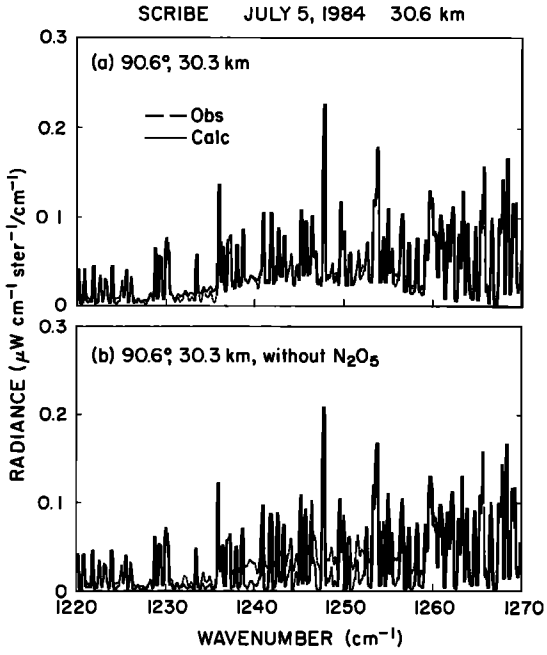

Fig. 2. Comparison of observed (dotted curves) and calculated (solid curves) atmospheric emission spectra in the N_2O_5 1220–1270 cm^{-1} region. Figures 2*a* and 2*b* are expanded versions of Figures 1*a* and 1*c*.

Residual background radiance was present at both observation angles (0.06 and 0.08 μW cm^{-2} sr^{-1}/cm^{-1} at 90.6° and 91.1°, respectively). For the present analysis the data were adjusted by applying a wavelength dependent correction, described by a linear function such that theory and observation agreed in the "mini windows" centered at 1227.0 and 1267.07 cm^{-1} and at the N_2O-CH_4 blend at 1268.31 cm^{-1}. These three positions are away from significant N_2O_5 absorption. The peak N_2O_5 cross section is 1.90×10^{-18} cm^2 at 1246 cm^{-1} (with no temperature correction), whereas the cross sections for the three calibration points are $\leq 1.5 \times 10^{-19}$ cm^2. Validity of the adjustment is apparent in the reasonable agreement to the CH_4 spectrum longward of 1268 cm^{-1} and insensitivity of the N_2O_5 quantification to the background radiance. Subsequently, a least squares fitting for N_2O_5 amounts over the 1240–1247 cm^{-1} interval (with N_2O and CH_4 fixed) was made. Recent measurements of N_2O_5 cross sections [*Cantrell et al.*, 1988*b*] show 1.79×10^{-18} and 1.82×10^{-18} cm^2 at 1246 cm^{-1} for 298 and 233K, respectively. Due to the small differences in comparison to the (room temperature) HITRAN value and the small temperature dependence, we did not adjust the HITRAN values.

The pressure-temperature profile used in these simulations was taken from a radiosonde ascent from White Sands Missile Range at 0800 MDT on the same day as the balloon flight. Mixing ratio profiles for the various constituents (except N_2O_5) are from *Smith* [1982].

Figures 1*a* and 1*b* show a comparison between the calculated (solid curve) and observed (dotted curve) emission for zenith angles of 90.6° and 91.1°, respectively. (Tangent heights are 30.3 km and 29.4 km.) The data have been smoothed by a triangular filter to 0.25 cm^{-1} resolution. The region is dominated by sharp emission lines of CH_4, N_2O, H_2O, and, to a considerably lesser extent, CO_2. At lower zenith angles there are also contributions from HNO_3 above ~1280 cm^{-1}, as well as from CF_4 (~1283 cm^{-1}) and $ClONO_2$ (~1292 cm^{-1}), but these molecules do not contribute appreciably at the zenith angles shown here. The broad, smooth emission feature in Figure 1*a* and 1*b* from 1230 to 1260 cm^{-1} is due to stratospheric N_2O_5. This can be seen from Figure 1*c*, which is the same as Figure 1*a*, except that no N_2O_5 has been included in the calculation. Figure 2 shows an expanded plot of the N_2O_5 1220–1270 cm^{-1} region from Figures 1*a* and 1*c*. Figure 3 presents the observed

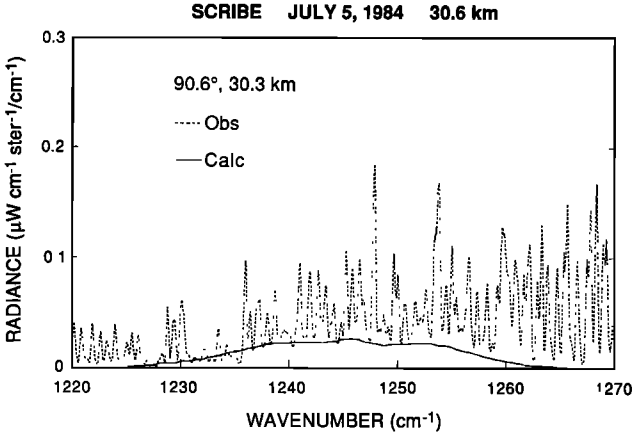

Fig. 3. Observed emission spectra (dotted curves) and theoretical calculation (solid curve) only including the N_2O_5 contribution.

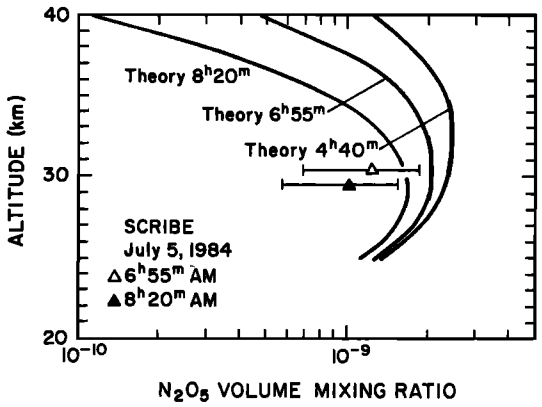

Fig. 4. One-dimensional photochemical-transport model (see text) mixing ratio profiles (solid curves) of N_2O_5 for predawn (0440 MST) and morning conditions used for comparison with the experiment. The triangles show the measured N_2O_5 mixing ratios 1.26 and 1.04 ppb, at the tangent altitudes 30.3 and 29.4 km.

radiance at 90.6° and a theoretical calculation which only includes the contribution due to N_2O_5.

The synthetic spectra of Figures 1*a* and 1*b* were computed using N_2O_5 profiles of the same general shape as the solid curves of Figure 4, which are generated as described below, multiplied by a scaling factor. The triangles in Figure 4 show the resulting N_2O_5 mixing ratios, 1.26 and 1.04 ppb, at the tangent altitudes of the two scans, 30.3 and 29.4 km, respectively. Theoretical N_2O_5 mixing ratios are 2.10 and 1.65 ppb for the corresponding times of 0655 and 0820 MST. The observed relative decrease in N_2O_5 is therefore 0.83, whereas the theoretical value is 0.79. The estimated accuracy of the absolute N_2O_5 measurements is ±45%. This is based on uncertainties in radiance calibration and pointing (10%), vertical slope of the theoretical N_2O_5 mixing ratios (10%), spectral line parameters (15%), and the N_2O, CH_4 profiles (10%). Error in the observed relative change is estimated as ±15% (due to partial cancellation of systematic errors).

The theoretical N_2O_5 mixing ratios curves were calculated by a one-dimensional photochemical transport model [*Cicerone et al.*, 1983]. The time dependent calculation extended between 10 and 80 km altitude. The pressure-temperature profile was that mentioned above, and the solar declination of +23° and the latitude of +33° matched that for the balloon flight.

Reaction rates for 81 two- and three-body gas-phase processes and 25 photolysis processes for 38 gaseous species follow that of the Jet Propulsion Laboratory (JPL 1987) [*DeMore et al.*, 1987], but with the *Cantrell et al.* [1988*b*] equilibrium constant for reaction (2). At 30 km at a temperature of 231K, the Cantrell and JPL 1987 equilibrium constants differ by 27%. However, for the geometry of the July 5 observation, the rate of thermal decomposition of N_2O_5 is slower than the diurnal average of N_2O_5 photolysis by a factor of 78, so the influence of the revised equilibrium constant upon the N_2O_5 mixing ratio is small. The total odd-chlorine (Cl + ClO + HOCl + $ClONO_2$ + HCl + ClO_2) mixing ratios are 2.17 and 2.61 ppb at 30 and 60 km, respectively. The J values at 30 km are 3.42×10^{-5} s^{-1} and 5.78×10^{-5} s^{-1} for N_2O_5 photolysis (reactions (3) and (4)) for 0655 and 0820 MST, respectively. The albedo value was 0.35, and J is insensitive to changes in the albedo (e.g., J equals 5.62×10^{-5} s^{-1} for an albedo of 0.25 at 0820 MST).

Since N_2O_5 is but one member of the NO_y family (N + NO + NO_2 + NO_3 + HNO_3 + HNO_4 + 2*N_2O_5 + $ClONO_2$), the theoretical value of N_2O_5 is related to the total NO_y mixing ratio. For the theoretical curves of Figure 2, NO_y is equal to 15.0 and 14.3 ppb at 40 and 30 km, respectively. Observations of *Russell et al.* [1988] for May 1985, sunset, 30°N latitude indicate NO_y near 16.7 and 15.2 ppb at 40 and 30 km, roughly 11% higher than our one-dimensional theoretical predictions.

The model N_2O_5 and NO_y profiles are reasonable, though they may not accurately represent the mixing ratio profiles of July 5, 1984, due to seasonal variations and model limitations. Differences between one- and two-dimensional models are illustrated, for example, in Figure 10-58 of *World Meteorological Organization* (WMO)/*NASA* [1986], in which the two modeling techniques at 30 km estimate different amounts of NO_y and, presumably, different amounts of N_2O_5. Despite such differences, the present measurement of the relative change of N_2O_5 during the morning hours is consistent with the temporal change of the one-dimensional calculation. Our observed early morning decline in N_2O_5 concentration is also consistent qualitatively (see equations (1)–(4)) with measured early morning increases in both NO and NO_2 [e.g., *Ridley et al.*, 1977; *Flaud et al.*, 1988; *Rinsland et al.*, 1988].

The present morning N_2O_5 results and the sunrise and nighttime N_2O_5 observations by *Toon et al.* [1986] and *Kunde et al.* [1988], all report N_2O_5 mixing ratios in the 1- to 2-ppb range near 30 km altitude. One sees that our observed mixing ratios at 0755 MDT and 0920 MDT are ~60% smaller than the values predicted by our model. *Kunde et al.* [1988] showed that their observed nighttime N_2O_5 is 20–30% smaller in comparison to a (different) photochemical model. However, the relative decrease of 0.83 over the 1.5 hours between the observations is consistent with that of 0.79 predicted by the model. The relative decrease in N_2O_5 concentration during the morning can be approximated by $D = \exp(-J\,\Delta t)$, where J is the average N_2O_5 photolysis rate over the time interval Δt. With $J = 4 \times 10^{-5}$ s^{-1} and Δt = 1 hour 25 min, D = 0.81, in good agreement with the detailed model results of 0.79. D is not sensitive to the actual N_2O_5 amount, and thus the absolute difference between models and measurements of N_2O_5 is less important than the temporal variations.

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